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# NOVEL TECHNIQUE FOR PREPARING A NANO-SILVER WATER SUSPENSION BY THE ARC-DISCHARGE METHOD

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**Abstract.** Studies on nanoparticles have become the target of major interest in modern science. Fabrication and characterization of silver nanoparticles has attracted considerable attention as a result of their significant applications in nano-technology and nano-biotechnology. The unique physical, chemical and mechanical properties of nanoparticles are the effect, among other things, of the high ratio of total surface area to their volume. Here we propose a means of preparing silver nanoparticles, suspended in pure water, using the arc-discharge method. The SEM image, size distribution, and UV-VIS spectrum are shown. The experimental results suggest that fabrication of silver nanoparticles in pure water without any surfactants and stabilizers by the arc-discharge method is relatively cheap and pollution free, and is a good alternative to other chemical methods. Our innovative studies demonstrate the safe and effective fabrication of silver nanoparticles free from any anions or cations in pure water.

## 1. INTRODUCTION

Metal nanoparticles have become an important target for modern chemistry, physics, technology and bio-engineering. Fabrication and characterization of silver nanoparticles has attracted considerable attention as a result of their significant applications in the fundamental sciences and nano-technology. The high surface-area-to-volume ratio of nanoparticles can create their unique physical, chemical, mechanical, and quantum size effect properties [1]. Their potential applications include catalysis [2], photographic processes [3], nano-detection by using surface-enhanced Ramam Scattering (SERS) [4], high-quality electrostatic precipitators, nano-photocatalysts in cosmetics, food, clothes, medicine, electrodes for MLCC (Multi Layer Ceramic Capacitors), silver fibers and others. Silver is a well-known bacteriostatic and poisonous agent for different bacteria and viruses [5]. No side effects were observed when using drugs based on metallic nano-silver in clinical trials.

In principle, current techniques for nanometer-sized metal particle preparation can be divided into two categories: physical and chemical. UV and IR radiation [6], aerosol technology and lithography, evaporation [7] or laser ablation [8] from metal bulk samples are used to generate nanoparticles by physical methods. Reduction of metal ions into neutral metal clusters is a commonly used treatment in chemical synthesis. This includes conventional chemical (one- or two-phase system), photochemical [9], sonochemical [10], electrochemical [11], and radiolytic reduction [12].

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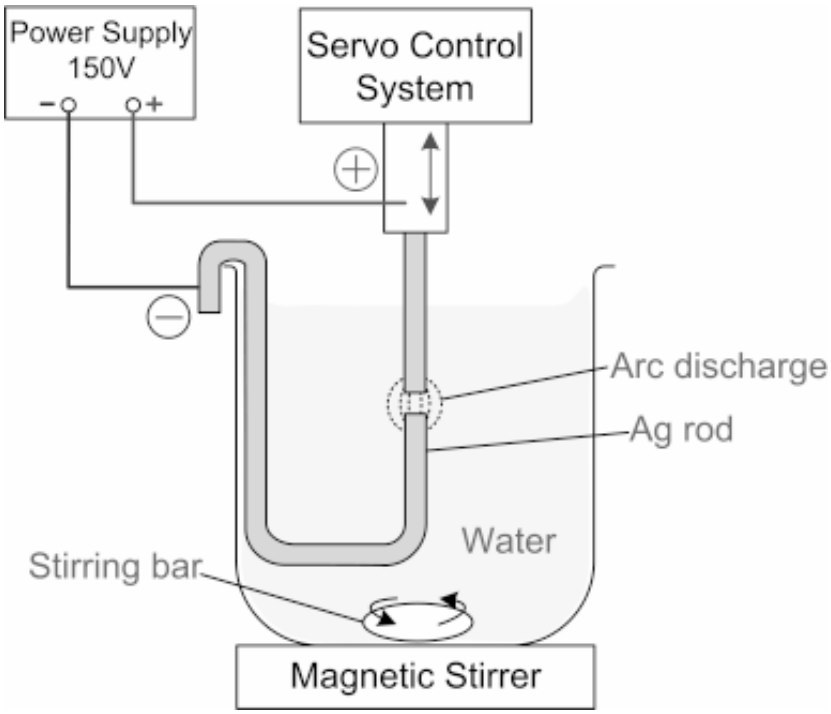


**Fig. 1.** The DC arc-discharge system.

The present paper describes a novel physical methodology of silver water suspension preparation by the arc-discharge method. Chemical methods for metal nanoparticle fabrication usually involve toxic chemicals, which can be dangerous to our environment. Although these methods may successfully produce pure silver nanoparticles, they require the use of stabilizers to protect the Ag nanoparticles against agglomeration. Additionally, these methods are usually expensive and potentially dangerous for the environment.

Our studies have revealed that the DC arc-discharge between silver electrodes in pure water is a good alternative method, and is not only a relatively cheap process, but also environmentally friendly. As far as we know, this method of Ag nanoparticles preparation by arc-discharge in pure water has not been published in scientific literature. During arc-discharge the temperature between electrodes can reach several thousand °C [13] and the Ag rods used as electrodes are etched in the water medium. The vaporized metal can be condensed more efficiently in the dielectric liquid than in the gas phase. Silver vapor condensed in water creates a stable Ag aqueous suspension. Well separated nano-sized Ag clusters in pure water seem to be thermodynamically stable for a long time.

## 2. EXPERIMENTAL

### 2.1. Materials

Silver wires (Gredmann, 99.99%) 1 mm in diameter and submerged in deionized water (pH = 5.8, conductivity = 0.8-0.9 μS) were used as electrodes.

### 2.2. Experimental system

The DC arc-discharge system (Fig. 1) consists of five main parts: *i)* two silver electrodes 1 mm in diameter, *ii)* a servo control system which maintains a constant distance between the electrodes, *iii)* a power supply system which controls the DC arc-discharge parameters, *iv)* a glass container with an electrode holder and deionized water to collect the silver colloids, *v)* a stirring system with magnetic stirrer and stirring bar.

### 2.3. Preparation of the silver nanoparticles suspension in pure water

The power supply system provides a stable pulse voltage for etching the Ag electrodes in pure wa-

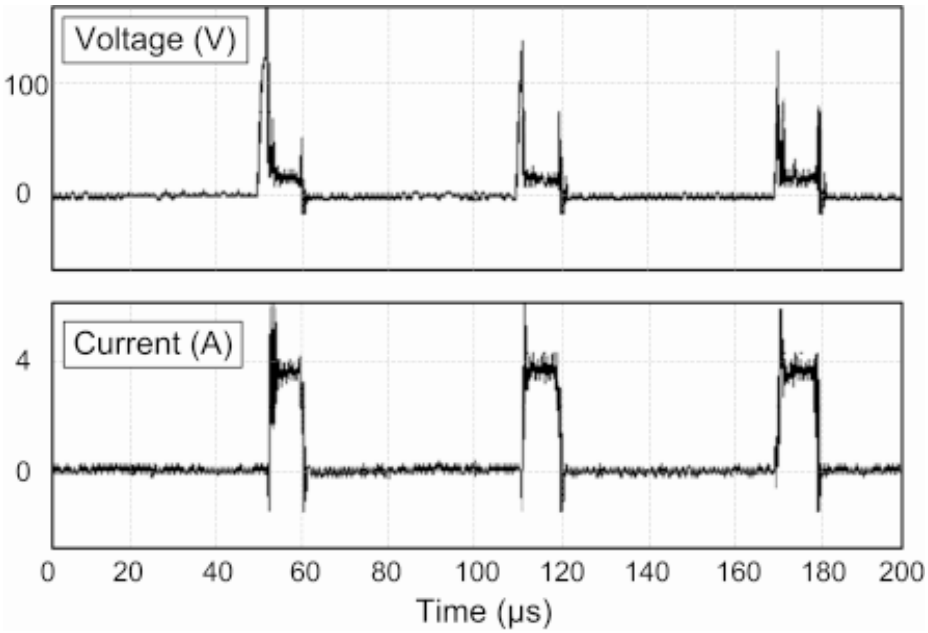


**Fig. 2.** Current and voltage pulses created by the DC arc-discharge system during etching of the silver electrodes.

**Fig. 3.** The sample of Ag nanoparticles suspended in pure water (pale yellow color).

ter. In order to ionize the aqua medium between the electrodes, the DC arc-discharge system provides a pulse voltage of 70-100 V for 2-3 ms and then maintains a pulse of 20-40 V for around 10 μs. At that moment the etching current can reach 4 A. The well-controlled on and off timing is shown in Fig. 2. The servo control system based on a feedback loop controls the gap between the electrodes which is equal to a few microns. The upper Ag electrode (usually the cathode) is held by the servo control system and the bottom one (usually the anode) is fixed by the electrode holder. The container with deionized water is maintained and stirred by using the magnetic stirrer at room temperature.

Silver wires are used as both the positive and negative electrodes. The pure silver wires are etched by the DC pulse arc-discharge in pure water. The parameters of the control system were chosen for optimal conditions of Ag nanoparticle production.

The governing parameters of this system such as the working voltage, selected current, pulse duration (on/off time), electrode gap, and temperature of the deionized water are crucial factors for nanoparticle production. During the arc-discharge, the surface layer of the Ag wires is evaporated and condensed in the water. The transparent solution converts to a characteristic pale yellow color (Fig. 3), and then a silver suspension is created.

The colloidal silver is then collected for inspection and analysis by the SEM technique and optical properties are studied by the UV-VIS spectrom-

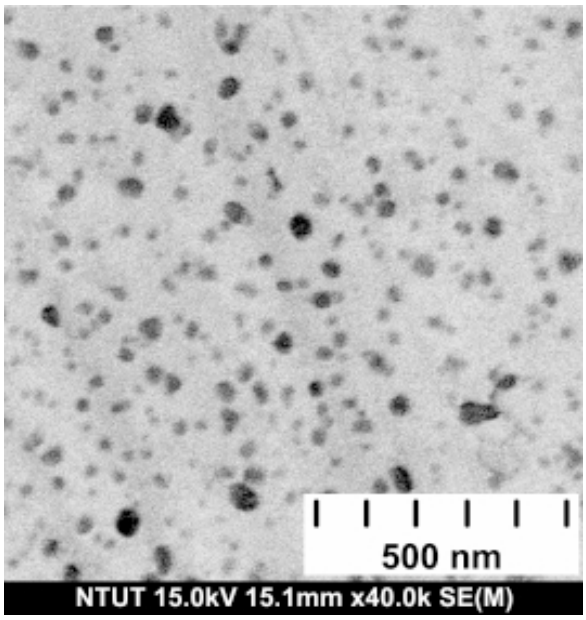


**Fig. 4.** The SEM image of the silver nanoparticles.

etry. The silver nanoparticles in water are stable for several months at room temperature without changing their properties.

## 2.4. Ag nanoparticles characterization

A Field Emission Scanning Electron Microscope (FE-SEM, HITACHI S4700) was used to demonstrate the silver nanoparticles' size distribution. Several drops of silver colloid were deposited on a conductive silicon wafer and then the sample was gently dried on a heating plate. The secondary electron SEM image was taken. To study the optical properties of the Ag nanoparticles, a double-beam UV-VIS spectrometer (9423UVA1002E Helios Alpha) was applied in the range of 200-700 nm. A 1 cm optical wide cuvette was used at room temperature.

## 3. RESULTS AND DISCUSSION

Fig. 4 shows the SEM image of the silver nanoparticles. Fig. 5 shows the size distribution of the silver nanoparticles calculated from the SEM image. Fig. 5 shows the TEM image of the silver nanoparticles. Fig. 6 shows the size distribution of the silver nanoparticles calculated from the SEM image. As can be seen, Ag particles 20-30 nm in size dominate.

During silver nanoparticle production by arc discharge in water, water decomposition (e.g. electrolysis) was also observed. This results in generation of gaseous hydrogen and oxygen, which appear in the water as small bubbles partly dissolved in the water medium. Hydrogen and oxygen start to interact with the newly prepared silver nanoparticles. Since hydrogen (molecular or atomic forms) does not adsorb on silver particle surfaces at room temperature [15], and also is not significantly dissolved in water, it is ultimately removed from the water suspension to the gas phase. However, oxygen (especially atomic) could adsorb and react with the silver surface at room temperature. We could also expect that during the arc-discharge process electrons are injected from the cathode to the silver nanoparticles, additionally saturated by atomic oxygen. Hence, Ag clusters could easily create hydrogen bonds with water particles in a water environment. Finally, negatively charged Ag nanoparticles are created in the water medium. Fig. 6 shows the typical UV-VIS absorption spectra for the silver nanoparticle suspension. Their maximum absorbance at around 396 nm has been confirmed by other authors as well [4,14].

Fig. 7 presents a model of the Ag nanoparticle, negatively charged micelle suspended in water. Due to hydrogen bonding, marked here by a dashed line, water molecules are bonded with the silver nanoparticles. Without any stabilizers or surfactants, negatively charged silver nanoparticles surrounded by water molecules are able to create a stable suspension. Such a silver colloid can be heated up to 100 °C without affecting its structure.

The DC arc-discharge method based on pure components, e.g. metal rods and deionized water, seems to be a promising alternative for metal nanoparticle fabrication. The system presented here can provide an effective and rapid mass-production method for silver nanoparticle preparation. No additives such as other solvents, surfactants, reducing agents or stabilizers are needed in this procedure. This simple and cheap DC arc-discharge process demonstrates high reproducibility in the fabrication of narrow range nano-sized Ag clusters.

## 4. CONCLUSIONS

1) The method of DC arc-discharge in pure water has been successfully developed for silver nanoparticle production. Silver nanoparticles in water without any surfactants or stabilizers are characterized as a stable colloid, which can be

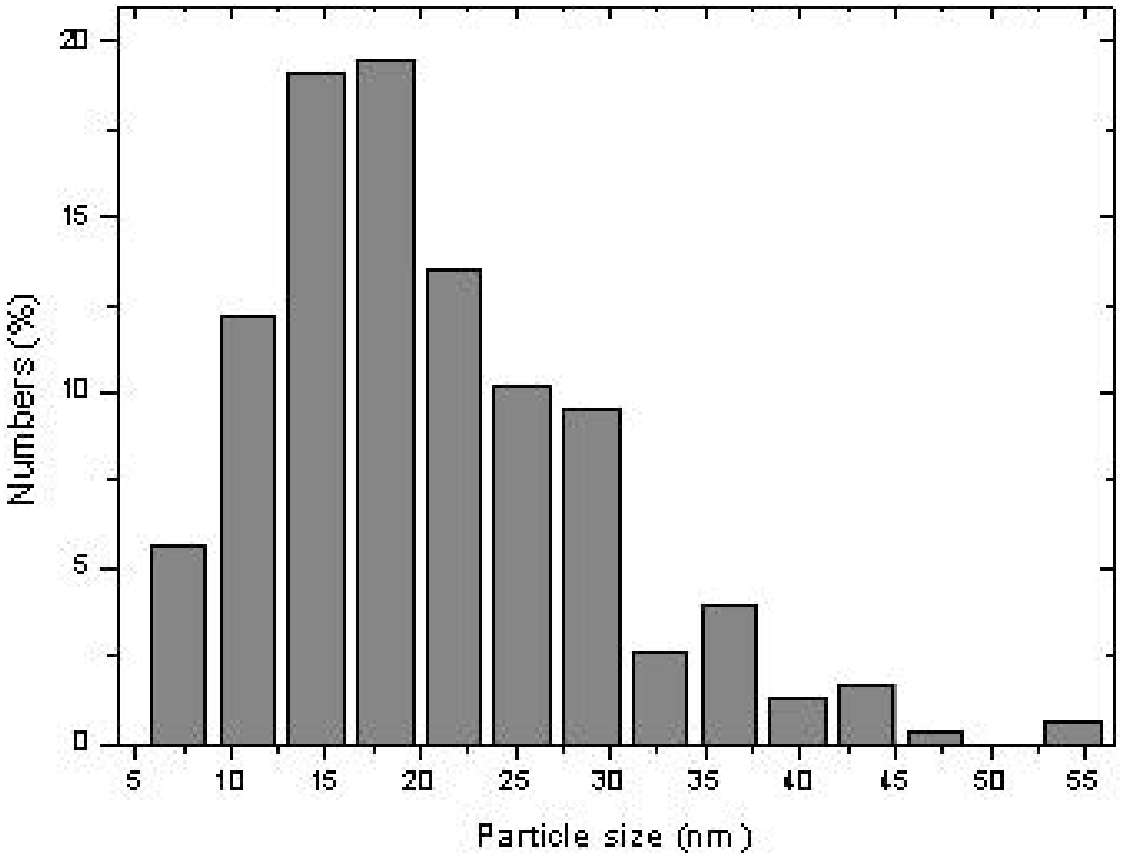


**Fig. 5.** The particle size distribution based on the SEM image.

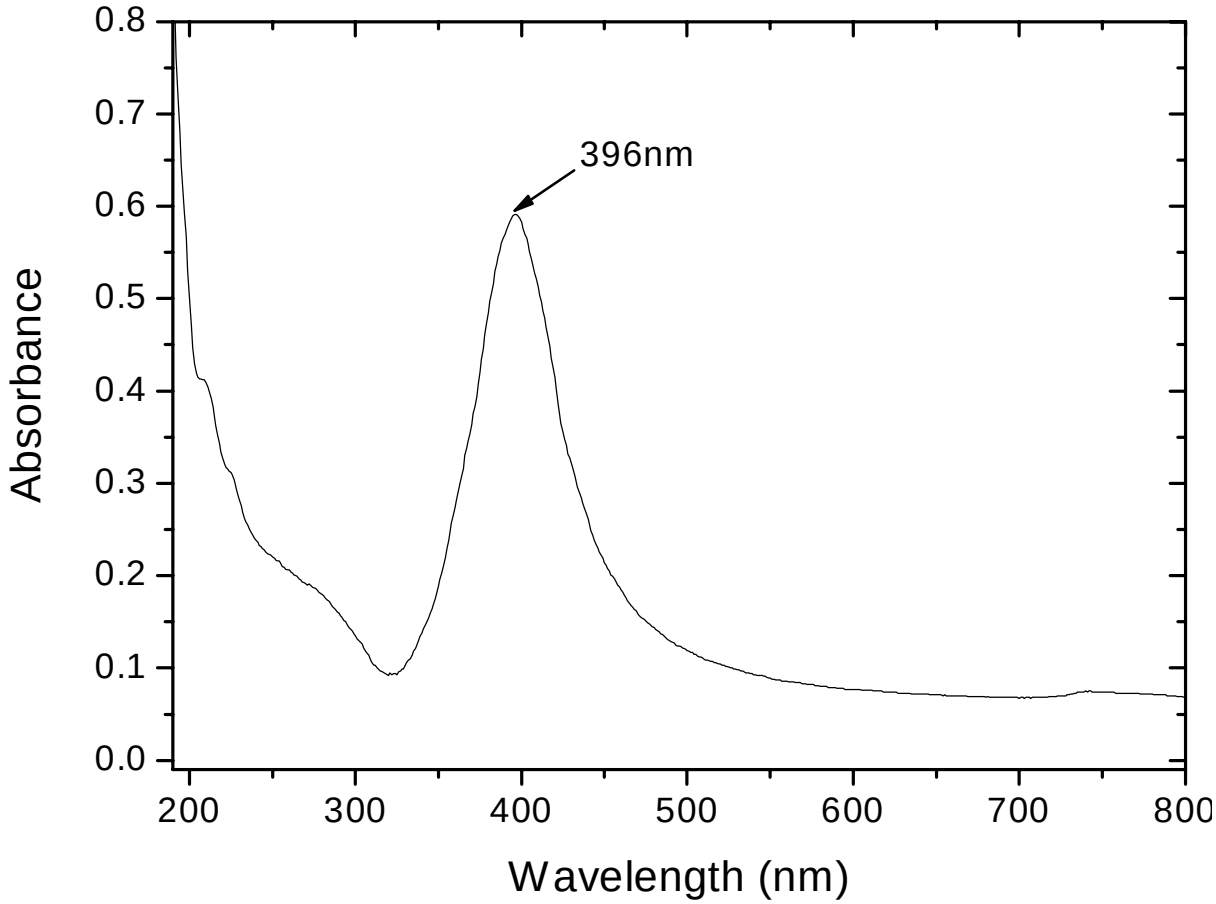


**Fig. 6.** The UV-VIS absorption spectra of the aqueous silver colloid.

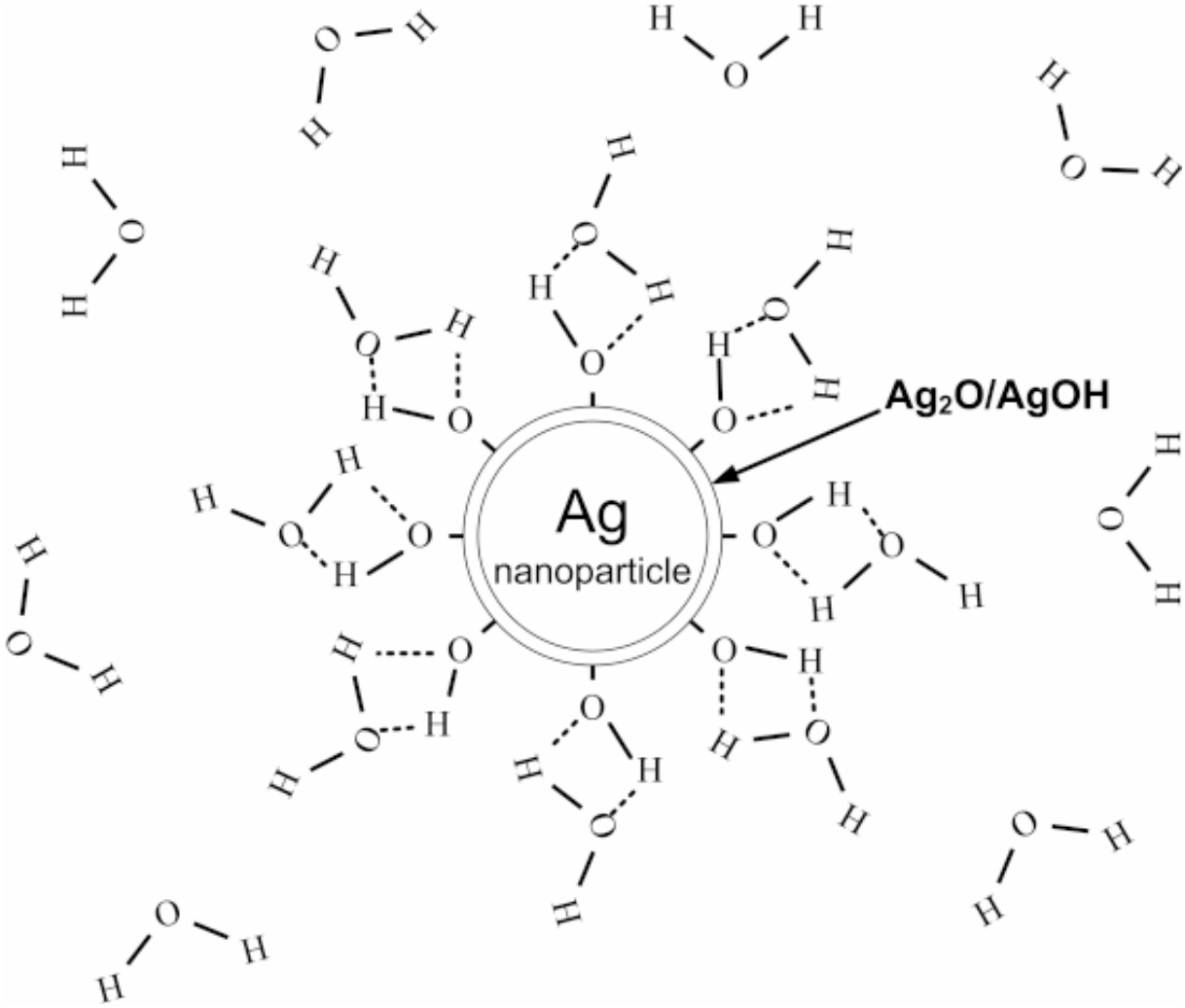


**Fig. 7.** Model of the negatively charged Ag nanoparticles suspended in water. Due to hydrogen bonding, marked here by (- - -), water molecules are bonded with the silver nanoparticles covered by silver oxide/hydroxyl layer.

stored in a glass container for a fairly long time at room temperature without visible sedimentation (no apparent precipitate).

2) The DC arc-discharge method in pure water is a cheap, effective, rapid and environmentally friendly process for silver nanoparticle production. This process can be applied as a method for mass production of narrow range nano-sized silver particles.
3) A novel and easy method for the preparation of silver nanoparticles, defined in nano-size and round in shape, using the arc-discharge method, was presented here.
4) Future studies in this area, such as time and temperature dependences, the relationship between voltage and current, and electric double layer formation will be continued for a better understanding of the Ag nanoparticle formation mechanism and stability in a water medium.

## ACKNOWLEDGMENTS

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## REFERENCES

[1] See for example: M. G. Bawendi, M. L. Steigerwald and L. E. Brus // *Annu. Rev. Phys. Chem.* **41** (1990) 477.
[2] T. Sun and K. Seff // *Chem. Rev.* **94** (1994) 857.
[3] See for example: H. H. Huang, X. P. Ni, G. L. Loy, C. H. Chew, K. L.Tan, F. C. Loh, J. F. Deng and G. Q. Xu // *Langmuir* **12** (1996) 909.
[4] S.-H. Park, J.-H. Im, J.-W. Im, B.-H. Chun and J.-H. Kim // *Microchemical Journal* **63** (1999) 71.
[5] See for example: H.-J. Lee, S.-Y. Yeo and S.-H. Jeong // *J. Mat. Sci.* **38** (2003) 2199.
[6] J.P. Abid, A.W. Wark, P.F. Brevet and H.H. Girault // *Chem. Commun.* **7** (2002) 792.
[7] G.T. Fei, R. Lu, Z.J. Zhang, G.S. Cheng, L.D. Zhang and P. Cui // *Mater. Res. Bull.* **32** (1997) 603.
[8] Y.H. Chen and S. Yeh // *Colloid. Surf. A* **197** (2002) 133.
[9] H. H. Huang, X. P. Ni, G. L. Loy, C. H. Chew, K. L. Tan, F. C. Loh, J. F. Deng and G. Q. Xu // *Langmuir* **12** (1996) 909.
[10] B. Li, Y. Xie, J. Huang, Y. Liu and Y. Qian // *Chem. Mater.* **12** (2000) 2614.
[11] Y. Y. Yu, S. S. Chang, C. L. Lee and C. R. C. Wang // *J. Phys. Chem. B* **101** (1997) 6661.
[12] A. Henglein // *J. Phys. Chem. B* **104** (2000) 2201.
[13] T.T. Tsung, H. Chang, L.C. Chen, L.L. Han, C.H. Lo and M.K. Liu // *Mater. Tran. The Japan Institute of Metals* **44** (2003) 1138.
[14] J. Zhu, X. Zhu and Y.C. Wang // *Microelectronic Engineering* **77** (2005) 58.
[15] R. Dus and E. Nowicka // *Progress in Surface Sci.* **74** (2003) 39.